LIGHT SCATTERING IN THE CRITICAL REGION

BY

HORACE ANTHONY CATALDI

B.Ch.E., The College of the City of New York, 1940
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

URBANA, ILLINOIS

1949

LIGHT SCATTERING IN THE CRITICAL REGION

BY

HORACE ANTHONY CATALDI

B.Ch.E., The College of the City of New York, 1940
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

URBANA, ILLINOIS

1949

ACKNOWLEDGMENT

The author expresses his appreciation to Professor H. G. Drickamer under whose direction this investigation was performed. He also thanks A. L. Babb for his assistance in assembling the equipment and in procuring the data, and the Shell Fellowship Committee for its financial aid during the last semester of the work.

R. UNIV. BIBLIOTHEEK LEIDEN

LIGHT SCATTERING IN THE CRITICAL REGION

Introduction

The original theory of light scattering in the critical region was developed by Smoluchowski (1) and Einstein (2) from the statistical fluctuations in density of independent, elemental volumes. As a consequence of this theory, the fractional light scattering is inversely proportional to the fourth power of the wavelength of the incident radiation, and becomes infinite at the critical point where $\delta p/\delta v = 0$. In order to remove this difficulty, Ornstein and Zernike (3) saw it was necessary to consider the relation between fluctuations in neighboring volumes by the introduction of a correlation coefficient. This leads to an expression for the fractional scattering which reduces to the Smoluchowski-Einstein equation for points away from the critical, where the correlation coefficient is small. At the critical point the scattering remains finite and becomes a function of the inverse square of the incident wavelength. Further, from scattering measurements at different wavelengths, it becomes possible to calculate a measure of cluster diameters as the critical point is approached. By a suitable manipulation of the original equation, this can be done without measurements of the incident light intensity.

The dependence of light scattering on wavelength has been measured by Keesom (4), Bhattacharya (5), and Andant (6) with results, which while not clear cut, are in substantial agreement with the theory of Ornstein and Zernike.

This investigation concerns the measurement of the 90 degree light scattering by ethylene, as a function of wavelength, density and temperature, and the calculation of representative cluster diameters near the critical point.

Results

An apparatus employing the 405 $m\mu$, 436 $m\mu$ and 546 $m\mu$

lines of a mercury arc lamp and a photomultiplier detector has been constructed for measuring the 90 degree scattering as a function of wavelength, density, temperature and height in the scattering bomb.

In the neighborhood of the critical point, 90 degree light scattering measurements reveal the existence of four regions:

1. A region where the light scattering depends on the inverse fourth power of the wavelength.
2. A region of increasing scattering and decreasing dependence on wavelength, beginning about a degree above the critical temperature and extending about to the critical temperature. The maximum scattering in this region is of the order of 100 times the initial value.
3. An abrupt decrease in scattering, possibly accompanied by absorption, occurring at a higher temperature for the shorter wavelengths.
4. A large and erratic increase in scattering apparently resulting from condensation.

The scattering observed upon cooling and reheating are identical, provided the temperature does not drop below the point for zero scattering or condensation.

The wavelength dependence of the light scattering is not completely described by any existing theory.

Applying the Ornstein-Zernike equation where it is possible, one calculates clusters of about 20 molecular diameters, more than a degree above the critical temperature. These clusters increase rapidly with further decrease in temperature.

BIBLIOGRAPHY

1. Smoluchowski, M. v., Ann. Physik, 25, 205 (1908).
2. Einstein, A., Ann. Physik, 33, 1275 (1910).

3. Ornstein, L. S., and F. Zernike, Proc. Acad. Sci. Amsterdam, 17, 793 (1914) ; Phys. Zeits., 27, 761 (1926).

4. Keesom, W. H., Ann. Physik, 35, 591 (1911).

5. Bhattacharya, D. K., Proc. Indian Assoc. Cultivation Sci., 8, 277 (1923).

6. Andant, M. A., Compt., rend., 176, 430 (1923) ; J. phys. radium, 5, 193 (1924).

VITA

The author was born on April 24, 1918, in Brooklyn, New York. He attended primary and secondary schools in Brooklyn, graduating from Bushwick High School in February, 1936. He received a New York State Scholarship and enrolled in the College of the City of New York. In February, 1940, he received the degree of Bachelor of Chemical Engineering. From April, 1941, to December, 1943, he was employed by the Navy Department as a physicist in their degaussing activities. From December, 1943, to March, 1946, he was employed by the Carbide and Carbon Chemicals Corporation in connection with the Manhattan Project, working first at Columbia University, and later at Oak Ridge, Tennessee. He left Oak Ridge, Tennessee, where he was Assistant Department Supervisor (Electronics), to enter the Graduate College of the University of Illinois in March, 1946. He served as research assistant for one year, and received the degree of Master of Science in Chemical Engineering in June, 1947. He was appointed to the Shell Fellowship in Chemical Engineering for one semester. He is a member of Tau Beta Pi and Sigma Xi.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549807_0098